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Corrosion inhibitor for heavy brines.

The corrosive effects of a heavy brine upon a ferrous metal are reduced by mixing a corrosion inhibitor with the brine, the inhibitor comprising at least one of monovalent and divalent salts of erythorbic acid, ferrous gluconate and sodium gluconate. A molybdate may be included. The brine solution can contain potassium, sodium, calcium or zinc halide salts. The corrosion inhibitor can be used in drilling, completion, packer and workover fluids.

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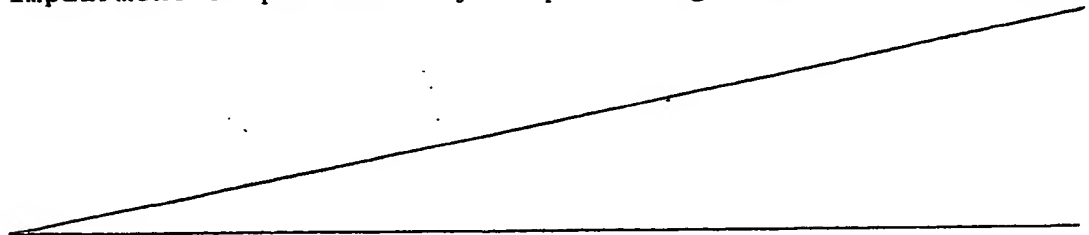
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CORROSION INHIBITOR FOR HEAVY BRINES

The present invention relates to a corrosion inhibitor for use in the protection of metals from the corrosive effect of heavy brines and particularly zinc halide brines employed in the drilling, completion and  
5 workover of well bores penetrating subterranean formations.

In the drilling of a well bore into a subterranean formation, it is necessary to cool the drill bit as it cuts into the formation and to remove the drill cuttings from the well bore. Normally, a drilling fluid is circulated down-  
10 wardly through the drill pipe within the well bore and outwardly through nozzles or openings in the drill bit. The drilling fluid then passes upwardly through the well bore annulus to the surface. Most drilling fluids contain  
15 suspended particles of hydrated clay in water. As the well bore is drilled, the suspended particles in the drilling fluid cause a filter cake to be formed on the face of the subterranean formation. The filter cake tends to seal off the formation and may result in the permanent reduction of permeability of the subterranean formation. To avoid  
20 impairment of permeability of producing intervals in a sub-



terranean formation, it is necessary to use a "clean" drilling fluid which will not damage the formation, but which has sufficient density to maintain formation pressures. Similarly, during well completion and workover operations performed on a well bore, it also is desirable to employ dense, but non-damaging fluids.

Commonly employed non-damaging fluids are high density aqueous brine solutions. For example, calcium chloride solutions can be produced having a density up to about 11.7 pounds per gallon of solution. Calcium bromide can be used to produce aqueous brines having a density of up to about 14.2 pounds per gallon. The incorporation of solid calcium chloride pellets in the brine permits a fluid having a density of about 15 pounds per gallon to be formed. When heavy brine solutions having a density greater than 15 pounds per gallon are required, aqueous solutions of zinc halides, such as zinc chloride or zinc bromide, normally are employed either individually or as blends with calcium halides. Most of the heavy brine solutions are highly corrosive to metals and, therefore, require the addition of expensive inhibitors to the solutions to protect metal surfaces contacted by the fluids. Many corrosion inhibitors are useful only at selected temperature levels or pH ranges for the various heavy brines and dilution, temperature changes or any change which effects the pH of the brine often results in loss of the corrosion inhibition. Particular problems arise in the selection of corrosion inhibitors for use in zinc halide-

containing heavy brine solutions. Many common corrosion inhibitors, such as organic thiophosphates, quaternized amines, polyphosphate esters, filming amines and the like form precipitates or are ineffective when admixed with zinc  
5 halide-containing heavy brine solutions.

It would be desirable to provide a corrosion inhibitor that is useful in retarding corrosion of metals in contact with heavy brine solutions and which does not precipitate from the solution upon addition or upon a change in  
10 the pH or temperature of the solution.

The discovery now has been made that the monovalent and divalent salts of erythorbic acid, when admixed in a sufficient amount with a heavy brine solution, will inhibit the corrosive effect of heavy brines upon metals in contact  
15 with the heavy brine solutions. More specifically, the salts of erythorbic acid, when admixed with a zinc halide-containing heavy brine solution, inhibit the corrosive effect of the brine upon metals and do not precipitate from the brine upon addition thereto or upon a change in pH or  
20 temperature of the solution.

The erythorbic acid salt can be added to the corrosive heavy brine solution in either solid or liquid form. The erythorbic acid salt also can be admixed with an effective amount of an alkali metal molybdate to provide corrosion inhibition to the heavy brine in excess of that  
25

depend upon the temperature, density of the brine and the particular compounds employed to produce the brine. In general, the quantity of erythorbic acid salt required to inhibit corrosion of a heavy brine increases with increasing  
5 brine density and increasing temperature levels. Preferably, sufficient erythorbic acid salt is admixed with the brine to provide a concentration in the range of from about 0.1 to about 25 ppb of the heavy brine solution. Preferably, the corrosion inhibitor of the present invention is present  
10 in an amount of from about 0.1 to about 10 ppb of the heavy brine solution.

The corrosion inhibitor of the present invention has been found to be particularly effective in inhibiting the corrosive effect of heavy brines containing zinc halides  
15 upon metal surfaces contacted by the heavy brine.

The effectiveness of the erythorbic acid salts as a corrosion inhibitor does not appear to be affected by the pH of the heavy brine solution. The corrosion inhibitor of the present invention is effective in acidic and about neutral  
20 solutions. Calcium and zinc halide salts are known to precipitate from solutions in which they are present when the pH level of the solution is increased to above about neutral. Therefore, the general pH range in which the corrosion inhibitor of the present invention is utilized is from about 0  
25 to about 8.

The corrosion inhibitor of the present invention, which comprises an erythorbic acid salt, is effective at

inhibiting corrosion of a metal in contact with a brine solution over a wide temperature range. The corrosion inhibitor is effective over a temperature range of from about ambient temperature to a level in excess of about 350°F.

5           The corrosion inhibitor of the present invention can be admixed with a heavy brine in a liquid or solid form. Preferably, the corrosion inhibitor is added as a liquid solution or as a powder which is readily solubilized in the heavy brine. Any conventional mixing apparatus can be utilized to disperse the corrosion inhibitor within the heavy  
10           brine solution. Alternatively, the corrosion inhibitor can be admixed with an aqueous fluid to which various salts are to be added to produce a heavy brine.

          The inhibited heavy brine solution can be used as  
15           hereinbefore described as a clean drilling fluid, a packer fluid, a completion fluid and in workover operations performed on a well bore which penetrates a subterranean formation.

          The effectiveness of the corrosion inhibitor of the  
20           present invention can be enhanced in some heavy brine solutions by the addition of an effective amount of an alkali metal molybdate to the erythorbic acid salt. A preferred molybdenum salt is sodium molybdate.

          The particular amount of the molybdate salt admixed  
25           with the heavy brine solution will depend upon the quantity of erythorbic acid salt, temperature, density of the brine and the particular compounds employed to produce the brine.

In general, the quantity of molybdate salt employed with the erythorbic acid salt is in the range of from about 0.1 ppb to about 2 ppb.

Corrosion of ferrous metals in contact with the  
5 brines primarily is caused by dissolved oxygen, organic and inorganic contaminants. The corrosion inhibitor of the present invention is believed by the inventors to reduce corrosion through several mechanisms. While the mechanism of the present invention is not known, it is believed the corrosion  
10 inhibitor can act or function as an antioxidant, as a reducing agent, as an oxygen scavenger and as a chelating agent in the brine solutions.

When organic contaminants degrade through an oxidative reaction, oxygen is incorporated into the system.  
15 Monovalent and divalent erythorbic acid salts present in a solution containing organic contaminants have been found to be more reactive toward the oxidative reaction and are preferentially consumed. This reaction prevents organic contaminant-induced corrosion of a ferrous metal in contact  
20 with the solution. As a reducing agent, erythorbates donate a hydrogen atom through either a change of valence state of an atom or in the removal of oxygen from the system by the formation of water. In combination with the reducing action, the erythorbates of the present invention also provide  
25 chelating action. Iron, for example, is kept in the  $\text{Fe}^0$  and  $\text{Fe}^{+2}$  states by a combination of reduction and chelating to prevent oxidation of the iron to the  $\text{Fe}^{+3}$  valence state.



To further illustrate the present invention, but not by way of limitation, the following examples are provided.

5

Example I

To illustrate the effectiveness of the corrosion inhibitor of the present invention in heavy brine solutions of differing densities, the following tests were performed. Various brine solutions were prepared by mixing sufficient quantities of calcium chloride, calcium bromide and zinc  
10 bromide in the form of saturated or near saturated industrial fluids in quantities of an aqueous solution to produce heavy brines having the densities set forth in Table I, below. Tared mild steel (AISI 4130) coupons then were immersed in quantities of the various brines which are main-  
15 tained at elevated temperatures for various periods of time to determine the relative corrosion rates of the steel coupons in the brines. Various quantities of the corrosion inhibitor of the present invention then are added to the remaining samples of the heavy brines and the corrosion  
20 tests are repeated with additional tared mild steel coupons. The inhibitor comprises sodium erythorbate in the tests. Upon completion of each test, the coupon is weighed and the corrosion rate of each coupon is determined. The relative reduction in the rate of corrosion resulting from use of the  
25 corrosion inhibitor of the present invention is determined by the following equation:

$$\% \text{ Corrosion Reduction} = \frac{C_1 - C_2}{C_1} \times 100$$

$C_1$  = Corrosion rate of sample in brine, mils/yr

$C_2$  = Corrosion rate of sample in brine with corrosion inhibitor, mils/yr

TABLE I

Test Solu- tion Density, ppg	Inhibitor Concen- tration, ppb	Dura- tion of Test, hrs.	Test Temper- ature, °F	Corro- sion Rate, mils/yr	Corro- sion Reduc- tion, %
15.0	0	168	150	2.595	-
15.0	1	168	150	0.692	73.3
15.0	0	164	150	2.330	-
15.0	2	164	150	0.619	73.9
15.0	0	168	275	7.328	-
15.0	1	168	275	6.706	8.5
15.0	0	168	275	7.328	-
15.0	5	168	275	1.289	82.4
15.0	0	168	325	218.17	-
15.0	2	168	325	51.05	76.6
16.5	0	168	150	2.748	-
16.5	1	168	150	0.459	83.3
16.5	0	166	150	1.751	-
16.5	2	166	150	0.359	79.5
16.5	0	168	150	1.789	-
16.5	3	168	150	0.511	71.4
16.5	0	168	300	18.302	-
16.5	5	168	300	3.339	81.8
16.5	0	166	350	23.97	-
16.5	2	166	350	21.574	10.0
16.5	0	166	350	23.97	-
16.5	3	166	350	6.44	73.2
16.5	0	166	350	23.97	-
16.5	5	166	350	1.97	91.8
18.5	0	164	150	3.762	-
18.5	2	164	150	1.290	65.7
18.5	0	70	300	153.0	-
18.5	5	70	300	132.0	13.7
18.5	0	166	300	126.5	-
18.5	10	166	300	26.4	79.2

Test blanks are run in each of the samples of uninhibited brine because of the different contaminants that can be present in the industrial chemicals used to form the brine samples.

5 The data set forth in Table I clearly illustrates the effectiveness of the present invention in inhibiting corrosion in heavy brines. Further, temperature stability

is demonstrated by effective operation at temperatures from about 150°F. to about 350°F. As illustrated by the data, corrosion rates increase as the temperature level and density of the brines increase. Therefore, as previously indicated, higher treatment levels are recommended for use at elevated temperatures with higher density brine solutions.

Example II

The effectiveness of the corrosion inhibitor of the present invention comprising sodium erythorbate is compared to other compounds to illustrate the unexpected nature of Applicants' discovery.

Corrosion proceeds at an exponential rate, the corrosion rate being very rapid initially and then decaying exponentially to a maximum corrosion plateau. When tests are run having different durations, it is difficult to relate the efficiency of the corrosion inhibitor to the quantity of chemical used per barrel of fluid to be treated because the temperature of the test oven, the duration of each test, the dissolved oxygen present in a fluid sample and the contaminants present in different fluid samples are not exactly the same.

Accordingly, a heavy brine is prepared having a density of 16.5 ppg by admixing calcium chloride, calcium bromide and zinc bromide into a nearly saturated aqueous fluid. The tests set forth in Example I then are performed employing a quantity of the various compounds indicated in Table II. The compounds are admixed with the brine as

aqueous solutions. The results of the tests are set forth in Table II, below.

Table II

Compound	Concentration, ppb	Duration of Test hrs	Test Temper- ature F°	Corro- sion Reduc- tion %
Potassium Citrate	2	165	150	2.4
Potassium Tartrate	2	165	150	-27.6 <sup>a</sup>
Sodium Fumarate	2	- b	-	-
Sodium Ascorbate	2	- b	-	-
Sodium Erythorbate	2	166	150	79.5
Aspartic Acid	2	168	150	-113
Sodium Aspartate	2 <sup>c</sup>	256	150	-140
Fumaric Acid	2	168	150	- 41
Gluconic Acid	2	168	150	- 55
Citric Acid	2	168	150	-202
Erythorbic Acid	2	168	150	- 20
Tartaric Acid	2	168	150	-243
Ascorbic Acid	2	168	150	- 0.4

a Negative value indicates corrosion rate was increased over rate of uninhibited brine solution

b Compound precipitated upon addition to brine

c 15.5 ml solution used is equivalent to 2 ppb of the salt

Surprisingly, the corrosion inhibitor of the present invention is effective in heavy brines while other antioxidants known for their ability to inhibit corrosion are either incompatible with the heavy brine or are not significantly effective in inhibiting corrosion of metals in contact with the brine. Sodium ascorbate, a stereoisomer of the corrosion inhibitor of the present invention, is incom-

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patible with any heavy brine containing a zinc halide. Also erythorbic acid, from which the salts comprising the corrosion inhibitor of the present invention are produced, is not effective as a corrosion inhibitor as indicated by the data set forth in Table II.

### Example III

To illustrate the effect of a molybdate salt upon the corrosion inhibitor of the present invention, the following test was performed. Various brine solutions are prepared having the densities set forth in Table III, below, by admixing calcium chloride, calcium bromide and zinc bromide into an aqueous fluid. Various quantities of the corrosion inhibitor comprising sodium erythorbate and sodium molybdate then are admixed with samples of the heavy brine solutions. The tests set forth in Example I then are performed. The results of the tests are set forth in Table III, below.

Table III

Test Solution Density, ppb	Inhibitor Concentration, ppb	Molybdate Concentration, ppb	Duration of Test, hrs	Test Temperature, °F	Corrosion Reduction, %
16.5	2	0	170	150	78.9
16.5	2	0.5	170	150	82.9
16.5	2	1.0	170	150	79.8
18.5	2	0	164	150	65.7
18.5	2	0.1	164	150	70.6
18.5	2	1.0	166	150	64.4

The use of the molybdate salt in combination with the erythorbic acid salt of the present invention in various

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heavy brines clearly can improve the effectiveness of the corrosion inhibitor, if the molybdate salt concentration is maintained within predetermined concentration levels.

5

Example IV

To illustrate the effectiveness of different monovalent and divalent salts of erythorbic acid, the following test was performed. A brine solution was prepared having a density of 16.5 lbs. per gallon by admixing calcium bromide and zinc bromide into an aqueous fluid. A quantity of various salts of erythorbic acid was admixed with a sample of the brine. The tests set forth in Example I then are performed. The results of the tests are set forth in Table IV, below.

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Table IV

Corro- sion Inhibi- tor	Inhibitor Concen- tration, ppb	Dura- tion of Test, hrs.	Test Temper- ature, °F	Corro- sion Rate, mils/yr	Corro- sion Reduc- tion, %
None	0	166	150	2.664	-
Sodium Erythorbate	2	166	150	0.755	71.7
Potassium Erythorbate	2	166	150	0.707	73.5
None	0	168	150	2.434	-
Sodium Erythorbate	1	168	150	0.404	83.4
Potassium Erythorbate	1	168	150	0.496	79.6
Calcium Erythorbate	1	168	150	0.417	82.9
Magnesium Erythorbate	1	168	150	0.419	82.8
None	0	165	150	2.751	-
Zinc Erythorbate	1	165	150	0.464	83.1
Ammonium Erythorbate	1	165	150	0.414	84.1
None	0	168	300	18.302	-
Sodium Erythorbate	5	168	300	3.339	81.8
Potassium Erythorbate	5	168	300	6.104	66.7
Calcium Erythorbate	5	168	300	10.240	44.1
Magnesium Erythorbate	5	168	300	5.279	71.2

The data set forth above clearly demonstrates the effectiveness of the monovalent and divalent salts of ery-



thorbic acid in inhibiting the corrosive effect of heavy brines, and particularly zinc halide-containing brines, upon metals in contact with the brines.

5 The salts of erythorbic acid are fairly stable in aqueous solutions, however, under acidic or aerobic conditions the salt can decarboxylate and be converted to furfural. The calcium salt of erythorbic acid has been observed to have a greater tendency to undergo this transformation than other salts of erythorbic acid. The reduced efficiency of calcium erythorbate at 300°F. in the preceding Example IV is believed to be attributable to the partial conversion of the compound to furfural. Furfural has biocidal rather than anticorrosion properties. Upon performing the test set forth in Example IV at 300°F. with calcium 10 erythorbate and 0.1 ppb sodium molybdate, the efficiency of the corrosion inhibition was improved from the level of 44.1% corrosion reduction for calcium erythorbate, alone, to a level of 54.5% corrosion reduction.

#### Example V

20 Various other metallic salts have been found to reduce corrosion in heavy brines, but generally at a lesser degree than the monovalent and divalent salts of erythorbic acid. Various brine samples are prepared as described in Example III and quantities of the various compounds are added to the brine samples. The data set forth in Table V 25 are the results of corrosion tests performed as described in Example I at a temperature of 150°F.

deionized water using an Orion oxygen probe manufactured by Orion Research, Inc., Cambridge, Massachusetts. Two (2) ppb of the various salts were added to each sample. Within two hours, the sodium erythorbate removed 70 percent of the dissolved oxygen in the deionized water while the ferrous gluconate removed 78 percent. Sodium gluconate removed only 16.7 percent in 3.5 hours. The comparative rate of oxygen removal is shown in the single drawing figure. The data set forth in the figure clearly demonstrates that oxygen scavenging is a function of the corrosion inhibitor in the mechanism of the present invention, but it is not the sole reason for the effectiveness of either the monovalent and divalent salts of erythorbic acid or the gluconate salts.

The various salts of erythorbic acid can be produced by the neutralization of erythorbic acid produced by acidifying sodium erythorbate. Sodium erythorbate is prepared from D-glucose by a combination of chemical and biochemical synthesis through the intermediate 2-keto-D-gluconic acid by treating with sodium methoxide as disclosed by the methods identified in The Merck Index, Ninth Edition. The potassium salt is produced by neutralization of erythorbic acid with potassium hydroxide. Other salts are formed by neutralization of erythorbic acid with ammonium hydroxide, magnesium hydroxide, zinc hydroxide, calcium hydroxide and the like.

CLAIMS:

1. A method of reducing or inhibiting the corrosion of a ferrous metal in contact with a heavy brine solution, which method comprises admixing with said brine solution an effective amount of a corrosion inhibitor comprising at least one monovalent or divalent salt of erythorbic acid, or sodium gluconate or ferrous gluconate.
2. A method according to claim 1, wherein said erythorbic acid salt is present in an amount of at least about 0.1 per pound barrel ( $0.28 \text{ kg/m}^3$ ) of said brine solution, preferably from about 0.1 to about 25 pounds per barrel ( $0.28$  to  $70 \text{ kg/m}^3$ ) of said brine solution, and most preferably from 0.1 to about 10 pounds per barrel ( $0.28$  to  $28 \text{ kg/m}^3$ ) of said brine solution.
3. A method according to claim 1 or 2, wherein said brine solution also contains at least one heavy salt selected from potassium halides, sodium halides, calcium halides and zinc halides.
4. A method according to claim 1, 2 or 3, wherein said brine solution has a pH level in the range of from acidic to about neutral.
5. A method according to any of claims 1 to 4, wherein said brine solution is at a temperature from about ambient to in excess of about  $350^\circ\text{F}$  ( $177^\circ\text{C}$ ).
6. A method according to any of claims 1 to 5, wherein said corrosion inhibitor also contains an effective amount of a molybdate salt, preferably from about 0.1 to about 2 pounds per barrel ( $0.28$  to  $5.6 \text{ kg/m}^3$ ).

7. A method according to any of claims 1 to 6, wherein the or each said monovalent or divalent salt of erythorbic acid is a member selected from sodium erythorbate, potassium erythorbate, calcium erythorbate, magnesium erythorbate, zinc erythorbate and ammonium erythorbate.

8. A corrosion inhibitor composition for use in heavy brine solutions having a density in excess of 10 pounds per gallon (1.2 g/ml), comprising at least one member selected from monovalent and divalent salts or erythorbic acid, sodium gluconate and ferrous gluconate.

9. A composition according to claim 8, which also contains a molybdate salt.

10. A composition according to claim 8 or 9, which is further capable of inhibiting corrosion of a zinc halide-containing heavy brine solution.

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DISSOLVED OXYGEN PRESENT,  
PARTS PER MILLION

